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Synthesis and Characterization of CO- and H_2S-Tolerant Electrocatalysts for PEM Fuel Cell

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ABSTRACT

The present state-of-art Proton Exchange Membrane Fuel Cell (PEMFC) technology is based on platinum (Pt) as a catalyst for both the fuel (anode) and air (cathode) electrodes. This catalyst is highly active but susceptible to poisoning by CO, which may be present in the H_2-fuel used or may be introduced during the fuel processing. Presence of trace amount of CO in the H_2-fuel poisons the anode irreversibly and decreases the performance of the PEMFCs. In an effort to reduce the Pt-loading and improve the PEMFC performance, we have synthesized a number of Pt-based binary, ternary, and quaternary electrocatalysts using Ru, Mo, Ir, Ni, and Co as a substitute for Pt. Co-catalytic activities were found for the elements Mo, Ru, and Ir. Both the ternary (Pt/Ru/Mo/C) and quaternary (Pt/Ru/Mo/Ir/C) metal catalysts in membrane electrode assemblies (MEA) outperformed pure Pt/C catalysts at all levels in presence of CO up to 100 ppm. Preliminary results suggest that by substituting Mo, Ru, and Ir in catalyst formulation, it is possible to reduce Pt-loading and increase CO-tolerance in PEMFC application. Comparison studies showed that the newly developed ternary and quaternary catalysts with lower Pt outperformed pure Pt catalyst in presence of CO-contaminated H_2 fuel. High performance at low Pt loading of less than 0.4 mg/cm^2 was achieved, thus exceeding the initial targets.

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EXECUTIVE SUMMARY

The Proton Exchange Membrane Fuel Cell (PEMFC) is one of the most promising power sources for stand-alone utility and electric vehicle applications. Platinum (Pt) catalyst is used for both fuel and air electrodes in PEMFCs. However, presence of CO and H_2S in H_2-fuel as contaminants adversely affects the electrocatalysts used at the anode of PEMFCs and decreases cell performance. The irreversible poisoning of the anode can occur even in CO and H_2S concentrations as low as few parts per million (ppm). In an effort to reduce the Pt-loading and improve the PEMFC performance, we synthesized a number of Pt-based bi-metallic, tri-metallic, and quaternary electrocatalysts using Ru, Mo, Ir, Ni, and Co as a substitute for Pt. By fine-tuning the metal loadings and compositions of candidate electrocatalysts, we were able to demonstrate that Pt metal loading can be significantly reduced by alloying Pt with metals like Ru, Mo, and Ir without compromising the cell performance. Using both conventional and ultrasonication method, we synthesized Pt-based binary, ternary and quaternary catalysts on XG72 carbon support. The metals that were alloyed with Pt in binary, ternary and quaternary combinations include Ru, Mo, W, Ir, Co and Se. From a large number of experiments, the catalytic activity of the synthesized catalysts were found to be in the order of Pt/Ru/Mo/Ir > Pt/Ru/Mo > Pt/Ru > Pt.

INTRODUCTION

In recent years, there has been growing interest in Proton Exchange Membrane Fuel Cell (PEMFC) technologies for down-to-earth applications because of its high power density, high efficiency and almost zero emission to the environment. The major focus on PEMFC technology is to develop fuel cell system for transportation applications, which require development of low cost cell components and reliable, high-purity H_2-fuel source [1, 2]. The PEMFC technology is attractive because of its low operating temperature and ease of start-up. Reformed methanol and liquid hydrocarbons are expected to be major fuel source in PEMFCs for terrestrial transportation application as envisioned in Vision 21 for the 21st century. The present state-of-art PEMFC technology is based on platinum (Pt) as a catalyst for both the fuel (anode) and air (cathode) electrodes. The electrochemical reactions that occur at the Pt-electrodes are:

Anode: $H_2 = 2H^+ + 2e^-$

Cathode: $O_2 + 4H^+ + 4e^- = 2H_2O$

The over all fuel cell reaction is:

$$2H_2 + O_2 = 2H_2O + \text{Energy}$$

A PEMFC potentially can achieve high power densities and high-energy efficiencies for the development of lightweight, small volume and low cost systems. Other attractive features include the absence of electrolyte leakage, tolerance to CO_2, and all solid-state materials. The present development of PEMFC is based upon ion exchange membranes (fluorinated sulfonic acid polymer or similar polymers) with platinum loaded carbon electrodes. Recent advances have addressed PEMFC problems related to the need for humidification of feed gases and removal of product liquid water to prevent flooding of the gas-diffusion cathodes. Another problem that may limit the ultimate utility of the PEMFCs is the susceptibility of poisoning the platinum (Pt) catalysts by the small levels of CO (carbon monoxide) and H_2S (hydrogen sulfide) present in the fuel stream. The current state-of-the-art PEMFCs require high purity gaseous H_2 (hydrogen) fuel feed stream and may not contain contaminants like CO and H_2S in concentrations in excess of a few ppm (parts per million). To achieve the desired low contaminant concentrations, a scrubbing system is usually necessary. Using these membranes, with a Pt-catalyst loading of 0.4 mg/cm^2 in H_2/O_2 fuel cells, a performance of 1.1 A/cm^2 current density with a cell voltage of 0.7 V is achievable [3,4].

In order to commercialize this environmentally sound source of energy/power system, development of suitable CO- and H_2S-tolerant catalyst is needed. The cost and reliability of electrocatalyst in PEMFCs are major impediments in commercial application [2,3]. Innovations are needed to reduce system costs and to enhance operating life before fuel cell can become commercially competitive with conventional power generating systems. Thus, to realize the benefits of PEMFC technology, two issues have yet to be resolved: (i) low cost electrocatalyst by reduced Pt-loading and (ii) high-performance electrocatalyst tolerant to CO and H_2S contaminated H_2-fuel [5].

In this work we propose to develop CO- and H_2S-tolerant electrocatalysts for PEMFC anode by combining platinum with additional metallic components. Ruthenium, a noble metal catalyst, is the preferred choice for providing CO tolerance. The sulfur tolerance may be imparted by a number of transition metals with molybdenum, cobalt, and tungsten as the leading candidates. Based on our current understanding and experience in the Pt-based bi-metallic and tri-metallic PEMFC electrocatalysts, we propose to further develop these electrocatalysts by fine-tuning the metal loadings and compositions to minimize the cost and optimize the catalyst activity and performance.

RESEARCH OJECTIVES

The objectives of this research are to:

- Synthesize novel candidate electrocatalyst materials
- Characterize the electro-catalytic activity in pure hydrogen half-cell studies
- Demonstrate electrocatalyst feasibility in contaminated hydrogen half-cell studies
- Demonstrate H_2/O_2 fuel cell performance with the improved electrodes in contaminated hydrogen environment

EXPERIMENTAL: MATERIALS & METHODS

Electrocatlysts Preparation

Metal catalysts and the MEA's for testing were prepared in house using standard procedures. The metal alloy catalysts for all the MEA's were maintained at 20-wt% and high surface area carbon (VULCAN XG-72) were used as the medium of support [6]. The in house metal alloy catalysts prepared by co deposition method is shown in Table 1.

Table 1. Synthesized in-house metal electrocatalysts*

Binary Catalysts	Ternary Catalysts	Quaternary Catalysts
Pt/Ru/C	Pt/Ru/Mo/C	Pt/Ru/Mo/Ir/C
Pt/Mo/C	Pt/Ru/Ir/C	Pt/Ru/Mo/Ni/C
Pt/Ir/C	Pt/Ru/Ni/C	Pt/Ru/Mo/Co/C
Pt/Ni/C	Pt/Ru/Co/C	
Pt/Co/C		

* Metal ratios were maintained at equal atom wt% with 20% metal loading.

Required metal precursors (Fisher Scientific.) usually chlorides and oxides were weighed stoichiometrically and mixed together at equal atomic wt%. This was followed by the stepwise addition of active components to reduce the metal chlorides in the precursors to the respective metals. A schematic of the catalyst preparation is shown in Figure 1. The metal alloy catalysts were prepared using the following simple procedure [7].

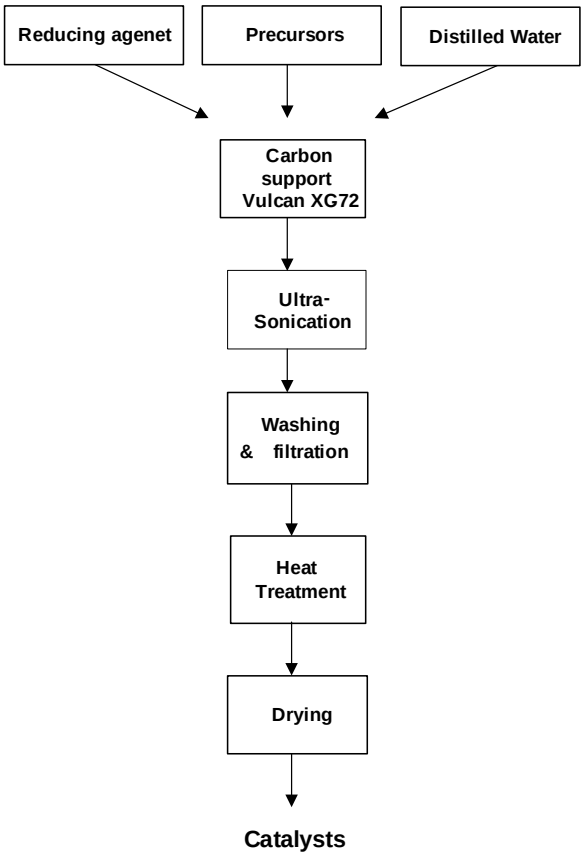

Figure 1. Schematic of the electrocatalysts synthesis method.

The metal precursors which consisted of chlorides and oxides were weighed in order to achieve equal atomic mass and dissolved in de-ionized water. A sodium bi-sulfate solution was added to the dissolved platinum chloride followed by careful drop-wise addition of .6M sodium hydroxide in order to maintain the pH of the solution to approximately 5 [8]. Next, 35 wt% hydrogen peroxide was added drop-wise and the rest of the dissolved metals and carbon black followed immediately. The mixture was then ultrasonicated (Misonix 3000) for approximately 45 minutes in order to disperse the active material more evenly on the carbon. After sonication, hydrogen was bubbled through the mixture at 60 °C in order to reduce the metal oxides onto the carbon. The solution was then filtered and washed and placed in an oven at 90 °C overnight. The powder was then subjected to hydrogen gas at 300 °C to reduce the metals further [9, 10]. These powders were ready to be made into MEAs and tested in the fuel cell. Commercially available 20 wt% Pt/C catalysts (Electrochem Inc.) were used as a reference.

Membrane Electrode Assembly (MEA) Preparation

MEAs were prepared from the synthesized electrocatalysts using a brushing technique. Nafion® 112 was used as the proton conducting polymer electrolyte. A controlled amount of Pt-alloyed catalyst was used in order to maintain a platinum loading of 0.4 mg/cm^2. A slurry was made using the catalysts, 5 wt% Nafion® solution, Polytetrafluraethylene (PTFE or Teflon), and an excess amount of distilled water. The Nafion® solution in the slurry was controlled at 0.6 mg/cm^2 as previously investigated in order to achieve maximum output in the fuel cell [11]. This slurry was well mixed and brushed onto pre-treated carbon paper (Electrochem Inc.). The wet electrodes were placed in the oven at 225 °C for 30 minutes, then at 350°C for approximately 30 minutes in order to evaporate all solvents. Each polymer membrane was treated first by boiling in 3.5 wt% hydrogen peroxide solution for 1 hour to remove organic materials. The membrane was placed in boiling 5N sulfuric acid which would allow the passage of hydrogen ions through the membrane. The membrane was boiled in distilled water for approximately 2 hours to remove any residual sulfuric acid. After the membrane was dry, the electrodes were hot pressed on each side of the membrane at 120 °C and 138 bars for 2 minutes. Figure 2 shows the schematic diagram of the MEA fabrication process used in this study.

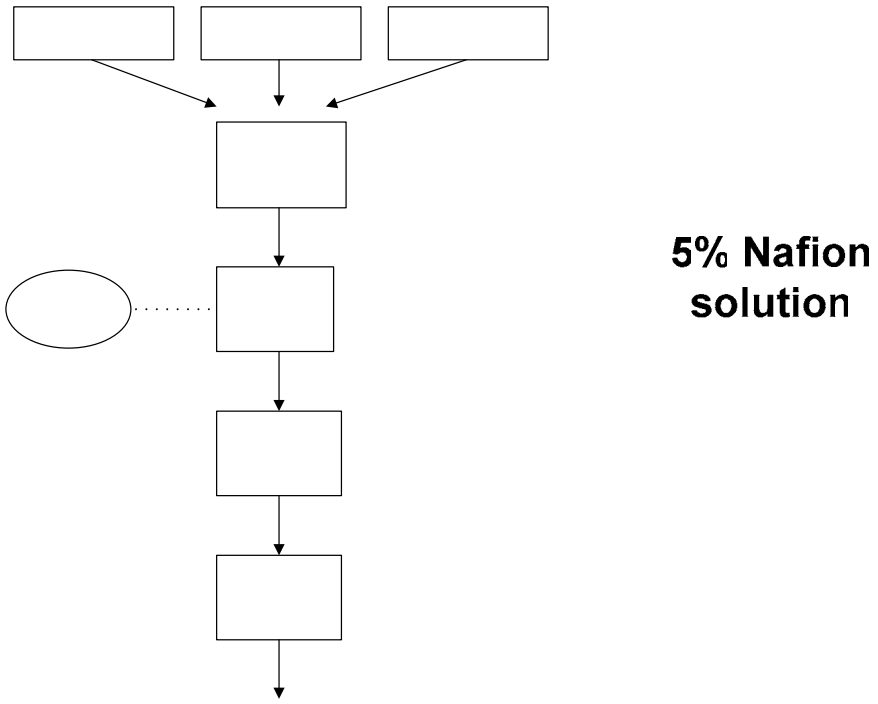

Figure 2. Schematic of MEA preparation.

Experimental Setup

The MEA was placed in a single cell of 5cm^2 area (FC05-01SP, Electrochem Inc,) and all necessary gas lines and electrical wires were connected to the fuel cell and test station. The DC current was read and controlled by an Agilent 6065B load box and interfaced with a computer using a National Instruments data GPIB card. The gas humidification and temperature control system (Fuel Cell Technologies, Albuquerque NM) along with the load box were controlled via the computer using LABVIEW software. The tubing leading from the test station to the fuel cell was wrapped in heating tape in order to maintain the humidified gas temperature and avoid flooding in the flow channels of the fuel cell. Purified air (UN 1049 from Air Products, Inc.) and hydrogen (UN 1002 from Air Products, Inc.) were used as the cathode and anode gas respectively for all of the polarization and impedance measurements. These gases along with carbon monoxide were controlled using Matheson Mass Flow Controllers and interfaced with the LABVIEW software. Water is a by-product of the chemical reaction taking place in the fuel cell; as a result water traps were placed in the exit streams of both the anode and the cathode of the

fuel cell. Back pressure regulators were also placed in the exit streams in order to monitor the pressure of the gases in the fuel cell. Figure 3 shows the diagram of the experimental setup.

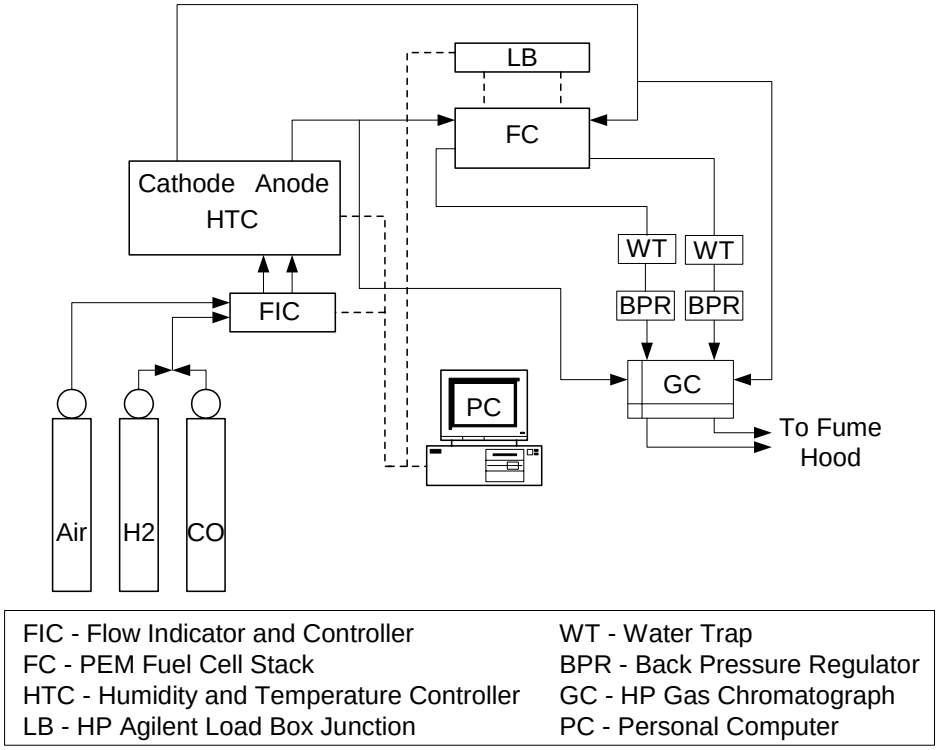

Figure 3: Schematic of test set-up of PEMFC for evaluation of electrocatalysts and MEASs.

Polarization Measurements

Polarization measurements are a common tool for electrochemical evaluation of synthesized electrocatalysts materials [12]. These measurements not only give the initial electrical output of the material but also test the durability of the fabricated MEA. Electrochemical evaluation of the PEM fuel cell can take place once the fabricated MEA is placed into the cell and all the necessary connections are made. Polarization measurements are made by utilizing the software to control the stoichiometric amounts of air and fuel to pass through the cell as well as to monitor the change in voltage while varying the current in the cell. Purified hydrogen, hydrogen containing 20 ppm of CO, and hydrogen containing 100 ppm CO were used as fuel in these measurements. A typical constant-voltage measurement is taken by obtaining the open circuit potential of the cell, then monitoring the voltage change with the increase in current density from zero to 1 A/cm^2 by increments of 0.10 A/cm^2. The control

software collected the data for each increment. Each candidate electrocatalyst was subjected to these tests.

AC Impedance Measurements

The AC Impedance system modulates the cell current by sending a small Sine wave to the DC Electronic Load external program input. This causes the cell current and voltage to change in response to the modulation signal. This voltage and current response was measured with the impedance system data acquisition card. The Sines correlation method was used to calculate the cell complex impedance from the waveforms measured. Electrochemical impedance spectroscopy (EIS) measurements were made with a frequency range of 100 mHz to 10 kHz at 10 points per decade. The voltage was varied between .45 V and .8V in increments of .05 V. The real and imaginary parts of the complex impedance responses were collected and plotted. The real response was on the x-axis and the imaginary response on the y-axis; this is known as a Nyquist plot. These plots will help us characterize the binary, ternary and quaternary metal catalysts synthesized in the laboratory.

RESULTS AND DISCUSSIONS

A number of PEM fuel cell electrocatalysts were prepared and evaluated in this work. This evaluation involved examining the surface morphology of the materials using SEM images, polarization of the electrocatalysts in the MEA, and ac impedance measurements of the electrodes. These methods were employed in order to determine how successful the synthesis method was and possibly the commercial feasibility of the materials.

Optimization of Parameters

Before starting the experiments, certain operational parameters had to be determined in order to obtain reproducible polarization curves from the PEM fuel cell. These parameters are fuel cell temperature, anode and cathode stream temperature, active metal loading in the catalysts, and the amount of Nafion impregnated into the MEA. The operating conditions and parameters were established based on our previous work [13]. These parameters are given in Table 2. All of the values allow the fuel cell to perform at its peak and give the best electrochemical performance.

Table 2. Optimum operating and experimental parameters

Parameter	**Value**
Active metal loading	0.4 mg/cm^2
Nafion® impregnation	0.6 mg/cm^2
Polymer electrolyte membrane	Nafion 112
Cathode/anode temperature	75 °C
Fuel cell temperature	85 °C

Materials Characterization

Electrocatalysts used in this study were synthesized from a modified technique; therefore, it is important that the physical aspects of the catalyst's surface be examined. A scanning electron microscope image of the material's surface will allow the viewing of the surface morphology of the materials at the nano-scale level. Figure 4 is a SEM image of an in-house Pt/Ir/C catalyst magnified at 30k.

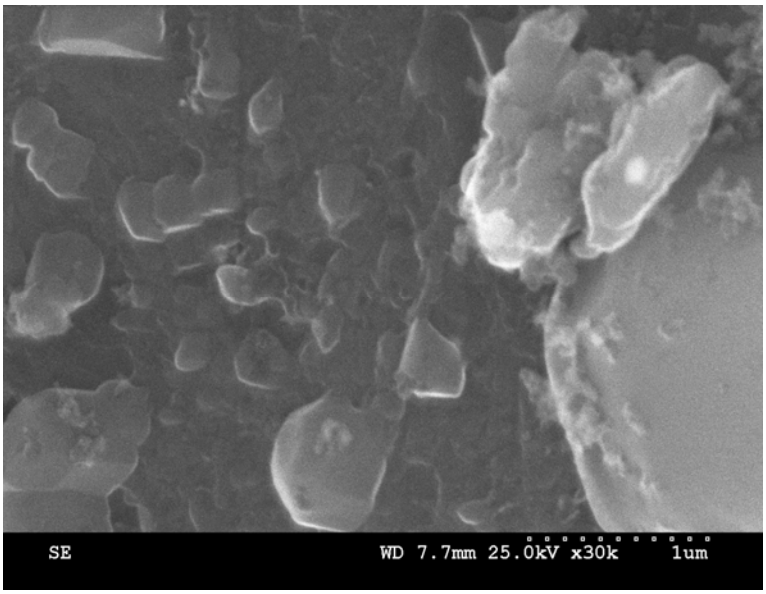

Figure 4. SEM image of in-house Pt/Ru/C catalyst (magnified 30,000 times)

The SEM image shows that the platinum and iridium were successfully deposited onto the support with a nanometer size diameter. Small active metal size is important because the materials can be dispersed more evenly on the Vulcan XG-72 carbon and thus more active sites

will be available for the H_2 oxidation and O_2 reduction reactions in the MEA [14]. More available active sites due to dispersion will also allow for better CO tolerance of the fuel cell. Scanning electron microscope images of other platinum based electrocatalysts can be found in the appendix.

Performance of Binary Metal Catalysts

One of the major obstacles in developing commercial PEM fuel cells is the cost of the cell due mostly to the noble metal platinum in the MEA of the cell. Figure 5 shows the current-voltage plot of a commercial MEA in the fuel cell with pure hydrogen, 20 ppm carbon monoxide and 100 ppm carbon monoxide in the feed stream.

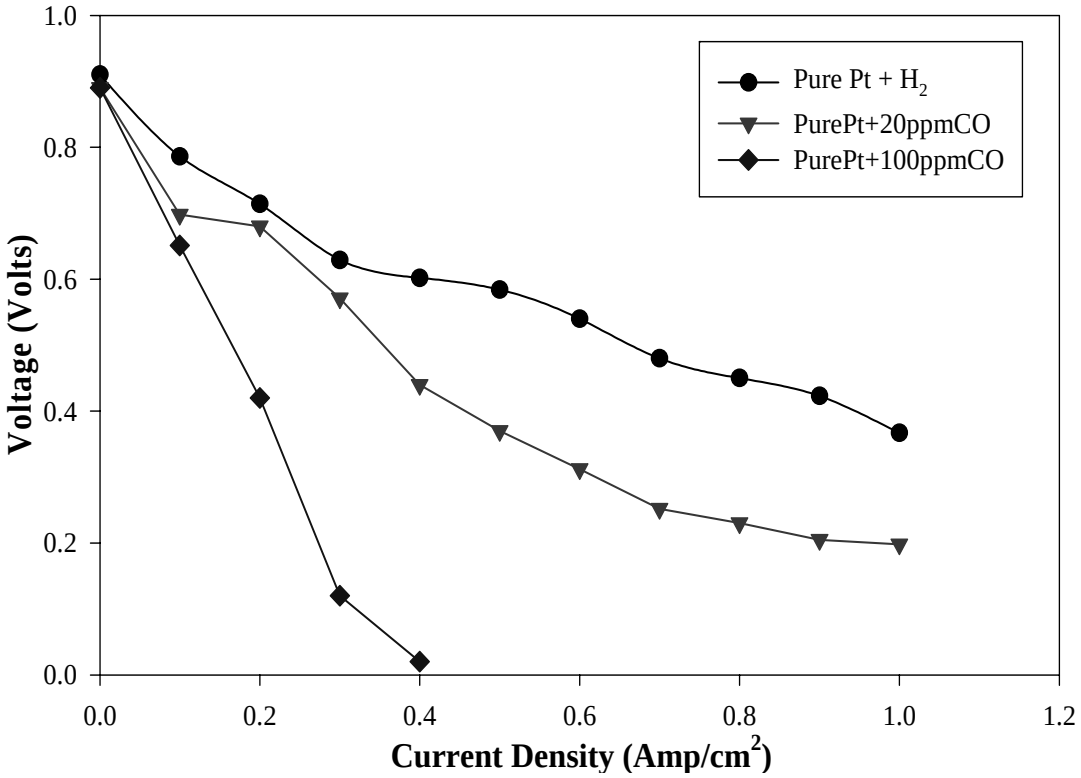

Figure 5. Current vs. voltage plots (polarization curves) of a commercial MEA with only platinum on carbon with pure H_2, 20 ppm CO and 100 ppm CO in the feed stream.

Lowering the amount of platinum while not decreasing the electrical performance of the cell would help relieve this problem. This can be accomplished by alloying the platinum with other non-noble metals. The following materials were used as binary catalysts in the fuel cell:

- 20-wt% Pt/Ru on Vulcan XG-72 carbon support
- 20-wt% Pt/Mo on Vulcan XG-72 carbon support
- 20-wt% Pt/Ir on Vulcan XG-72 carbon support
- 20-wt% Pt/W on Vulcan XG-72 carbon support
- 20-wt% Pt/Se on Vulcan XG-72 carbon support

Figure 6 shows the co-catalytic activity of the non-noble metals in these binary catalysts with pure hydrogen in the anode feed. The results show that platinum alloyed with ruthenium had the best performance in the fuel cell which is consistent with the literature. The next most active catalyst is the Pt/Mo/C catalyst followed by the Iridium, Tungsten, and Selenium alloyed catalysts. The Pt-Ru system has been known to be the most active binary electrocatalyst in a PEM fuel cell; this is largely due to ruthenium's ability to perform the oxidation reduction reaction within platinum's cubic structure [15]. Platinum alloyed with molybdenum is closely behind the Pt/Ru/C catalysts in performance. Molybdenum has enhanced co-catalytic activity because it is likely to form a Mo bronze with redox, which can be attributed to rapid change in the oxidation state [16].

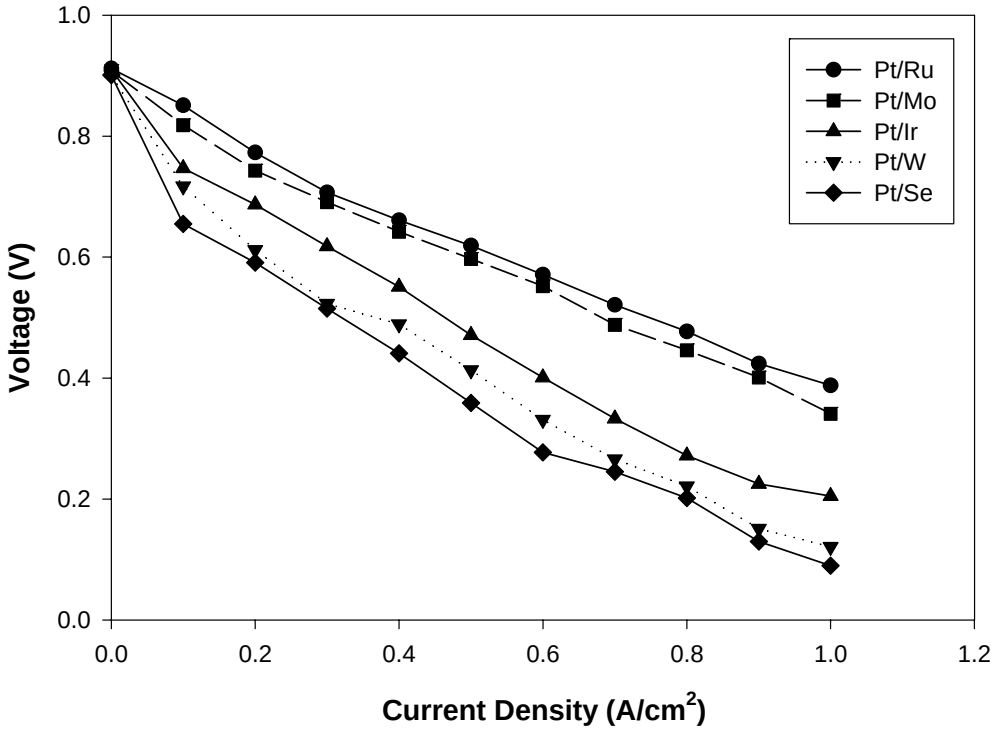

Figure 6. Current vs. voltage performance curves of the MEAs with binary electrocatalysts (20 wt%) with pure H_2 in the feed

Figure 7 shows the comparison of in-house binary catalysts synthesized by the method described in this work to binary catalysts prepared by a similar method in a previous work. The performances of the platinum alloyed materials follow the same trend; however the catalysts prepared with sonication have a slightly higher voltage at a given current density. This is due in part to better dispersion of the active materials on the carbon support caused by the ultra-sonication process. Better dispersion leads to smaller particle size and more accessibility of the active sites for the hydrogen oxidation and oxygen reduction reaction taking place in the MEA of the fuel cell.

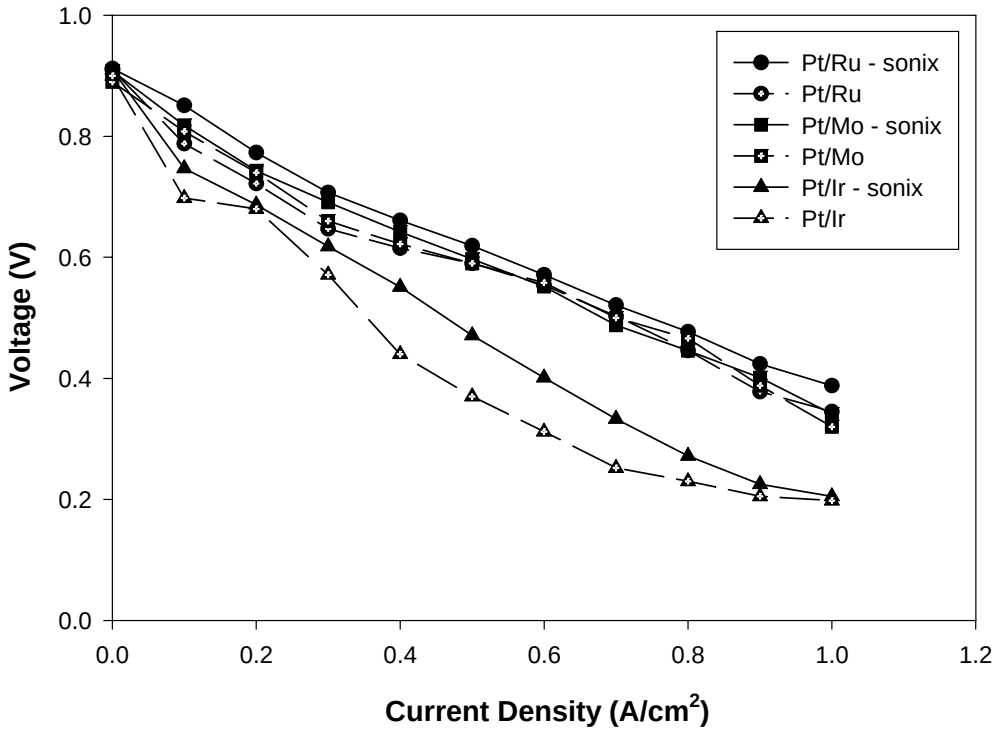

Figure 7. Performance comparison of binary catalysts (20 wt%) made with sonication (sonix) and without sonication during the synthesis process with pure H_2 in the anode feed stream

Performance of Ternary Metal Catalysts

Based upon the top performing binary co-catalytic system (Pt/Ru), ternary metal catalysts were synthesized and tested. The following three-metal candidates were fabricated into MEAs and tested:

- 20 wt% Pt/Ru/Mo on Vulcan XG-72 carbon support
- 20 wt% Pt/Ru/Ir on Vulcan XG-72 carbon support
- 20 wt% Pt/Ru/W on Vulcan XG-72 carbon support

- 20 wt% Pt/Ru/Se on Vulcan XG-72 carbon support

The polarization curves for the above materials are shown in Figure 8. This graph shows that molybdenum alloyed with Pt/Ru is the most active catalyst followed by iridium and tungsten. This trend also follows those of other research findings. In some cases tungsten has been found to be more active than molybdenum in a ternary metal catalyst system [7]. The difference in the findings here may be due to the synthesis method employed in order to deposit the active metals onto the carbon support. Proprietary reduction methods have been used in order to deposit nanometer sized active metals onto their supports which could cause the active metals in a ternary metal catalyst to alloy differently from the method employed in this work. Figure 8 also shows that Pt/Ru alloyed with Mo, Ir, and W exhibit a similar voltage reading at a current density of 200 mA/cm^2. However, at higher current densities Pt/Ru/Mo has the better voltage reading than the other two metals.

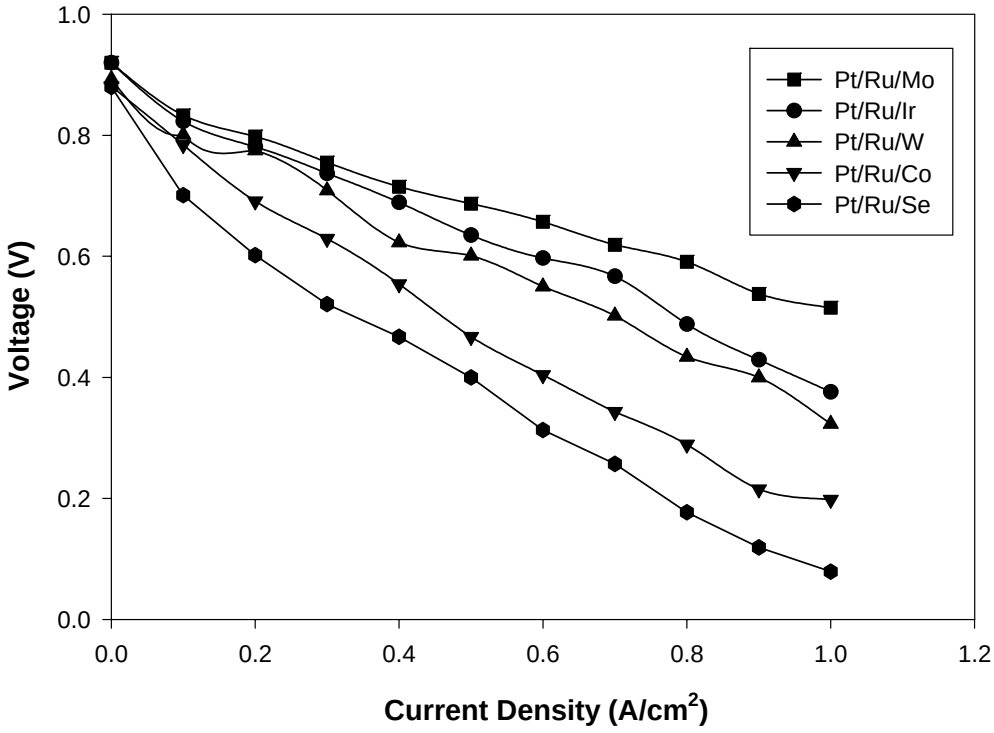

Figure 8. Current vs. voltage curves for ternary electrocatalysts (20 wt%) with pure H_2 in the anode feed stream

Figure 9 shows a comparison of the ternary catalysts synthesized by the method described in this work and those same ternary catalysts synthesized by a similar method without the sonication step. Once again, those catalysts with the sonication step exhibited a slightly higher voltage at the same current density for those without sonication. Better dispersion of the three active metals on the carbon support leads to a better voltage reading from the MEAs. The sonication step allows the reducing agent to successfully deposit the active metals Pt, Ru, Ir, Mo, and Co in their elemental form from their precursors on the support and allow for better co-catalytic activity in the fuel cell.

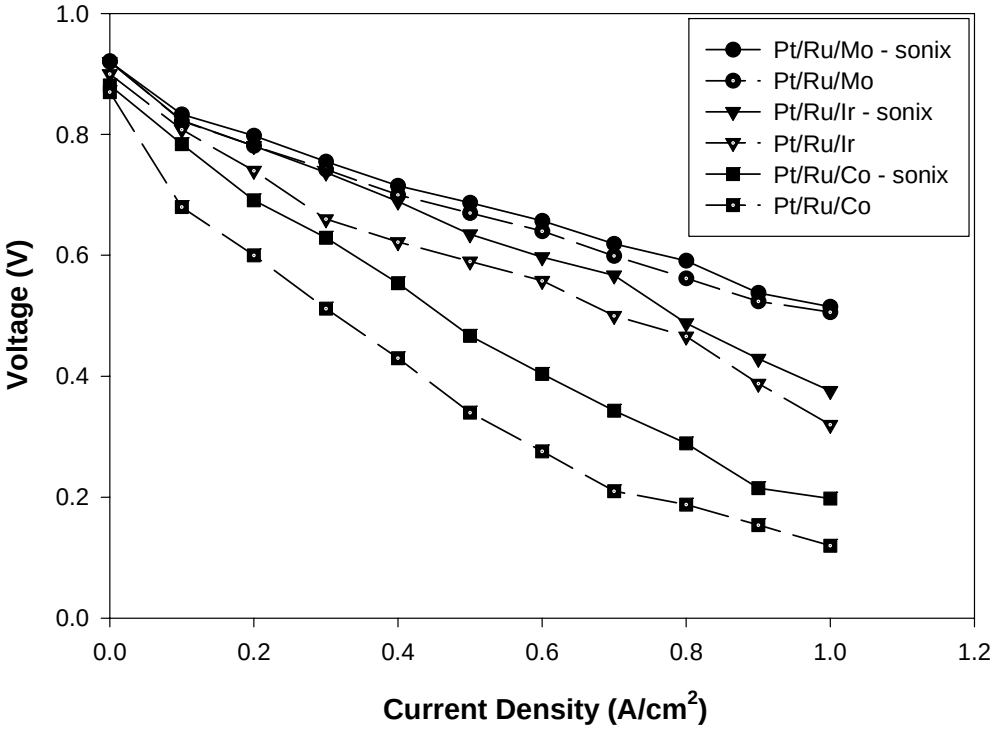

Figure 9. Performance comparison of in-house ternary metal catalysts (20 wt%) synthesized with sonication and without sonication with pure H_2 in the feed

CO Tolerance of Ternary Metal Catalysts

In order to make PEMFC more suitable for practical commercial applications a robust electrocatalyst for the MEA must be developed. While fuel cells operating on hydrogen produced from a reformer may be more practical, their performance decreases dramatically because of the inclusion of a few parts per million of carbon monoxide in the stream. Carbon

monoxide chemisorbs onto the surface of the platinum in the electrocatalyst, poisoning the surface for H_2 oxidation and greatly reducing the electrical output of the cell. Research in the area of hydrocarbon reforming is geared toward developing catalysts which can convert the hydrocarbons into hydrogen with little to no CO at a relatively low temperature [17]. But developing CO tolerant electrocatalysts can help alleviate some of the burden in reforming while also lowering the total platinum loading in the catalysts.

The same ternary metal candidates were used for the CO tolerance study as those used in the previous section. The amount of CO in the stream was varied from 20 ppm to 100 ppm in order to simulate operation from reformate gas. Figure 10 displays the polarization curves for the ternary catalysts with pure H_2 and 20 ppm CO in the feed.

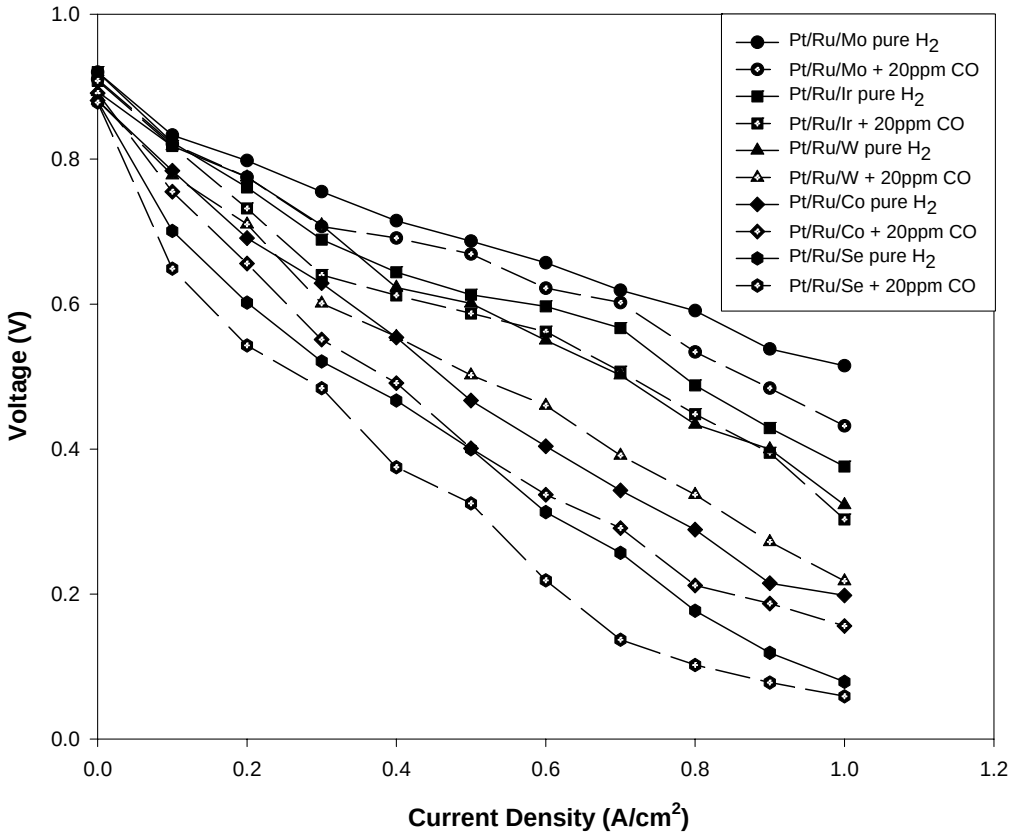

Figure 10. CO tolerance of ternary metal (20 wt%) catalysts with pure H_2 and 20 ppm CO in the H_2-feed

The results show that Pt/Ru alloyed with Mo, Ir and W has very good co-catalytic activity towards carbon monoxide oxidation reaction in an MEA. The figure also shows that there was

not much of a drop off in performance with the Pt/Ru/Mo, Pt/Ru/Ir and Pt/Ru/W catalysts when 20 ppm CO is added to the feed stream. The increased CO tolerance of the Pt/Ru/Mo catalyst can be attributed to the ability for Mo to promote the CO oxidation process at very low electrode potentials [7]. This was attributed to oxygen transfer from molybdenum oxyhydroxide species with only the OH species of the oxyhydroxide states, predominantly $MoO(OH)_2$), being reactive with absorbed CO [15]. There was a significant loss in performance of the cell when 100 ppm of CO was added to the feed for all of the ternary catalysts.

Figure 11 shows the polarization curves for the ternary catalysts with 20 ppm and 100 ppm of CO in the H_2 stream. Even the most active ternary catalysts at 20 ppm CO, the Pt/Ru/Mo catalyst, did not produce a significant voltage output beyond 600 mA/cm^2 with 100 ppm CO in the feed.

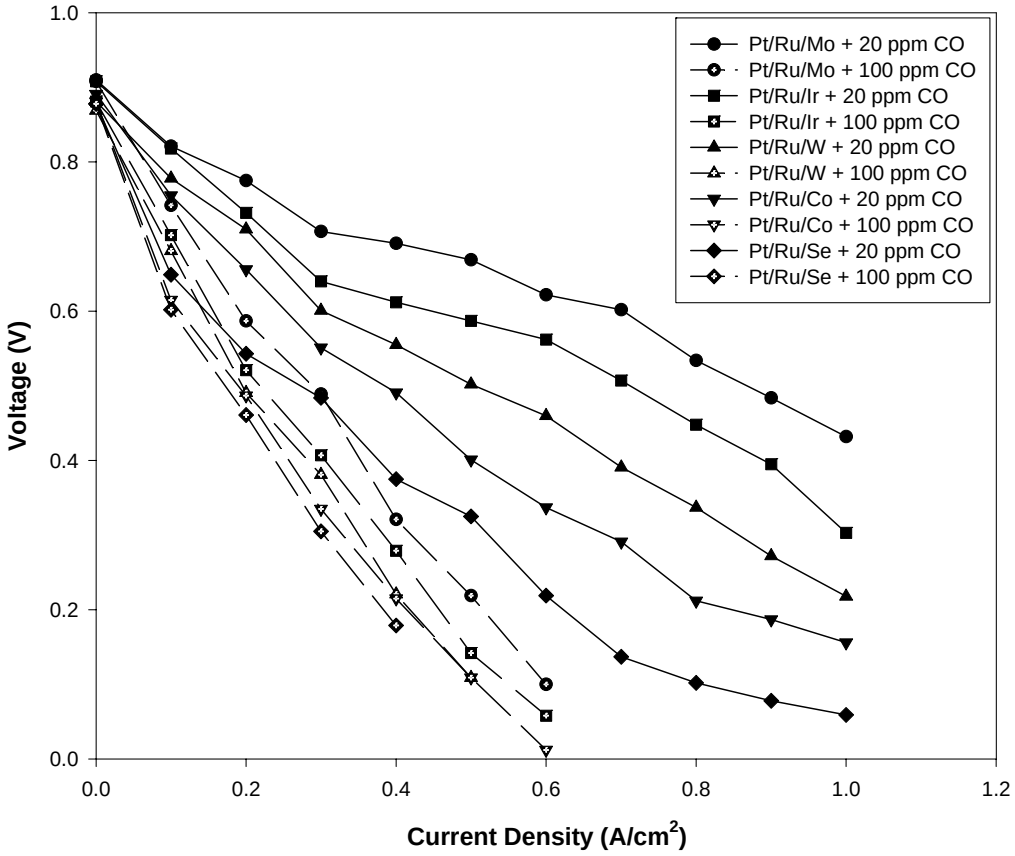

Figure 11. CO tolerance of ternary metal (20 wt%) catalysts with 20 ppm and 100 ppm CO in the H_2-feed

Performance of Quaternary Metal Catalysts

Not much work has been published on the study of platinum-based quaternary catalysts for PEM fuel cells. After good results with the ternary metal catalysts, it seemed of interest to carry out the similar investigation using the metal alloys from the binary and ternary metal systems. As with the previous trimetallic and bimetallic catalysts, an atomic ratio of 1:1:1:1 of active metal on the carbon support was used for the candidate catalysts. This would not only allow for the reduction in platinum loading, but it would also give a better dispersion of the active material on the support. Better dispersion would lead to more co-catalytic activity of the alloyed catalysts in the MEA of the fuel cell.

The better performing alloyed catalysts from the ternary and binary systems were chosen to be studied as quaternary catalysts:

- Pt/Ru/Mo/Ir on Vulcan XG-72 carbon support
- Pt/Ru/Mo/W on Vulcan XG-72 carbon support
- Pt/Ru/Mo/Co on Vulcan XG-72 carbon support
- Pt/Ru/Mo/Se on Vulcan XG-72 carbon support

Figure 12 shows the current-voltage performance plots for these quaternary catalysts with pure hydrogen in the feed. This graph shows that the Pt/Ru/Mo/Ir/C electrocatalyst gave the best performance of the candidates followed by Pt/Ru/Mo/W/C. While the overall electrical output of the fuel cell may not have increased significantly when compared to the ternary catalysts, the additions of Ir and W allowed for lower platinum loading in the MEA and thus reduced the overall cost of the fuel cell.

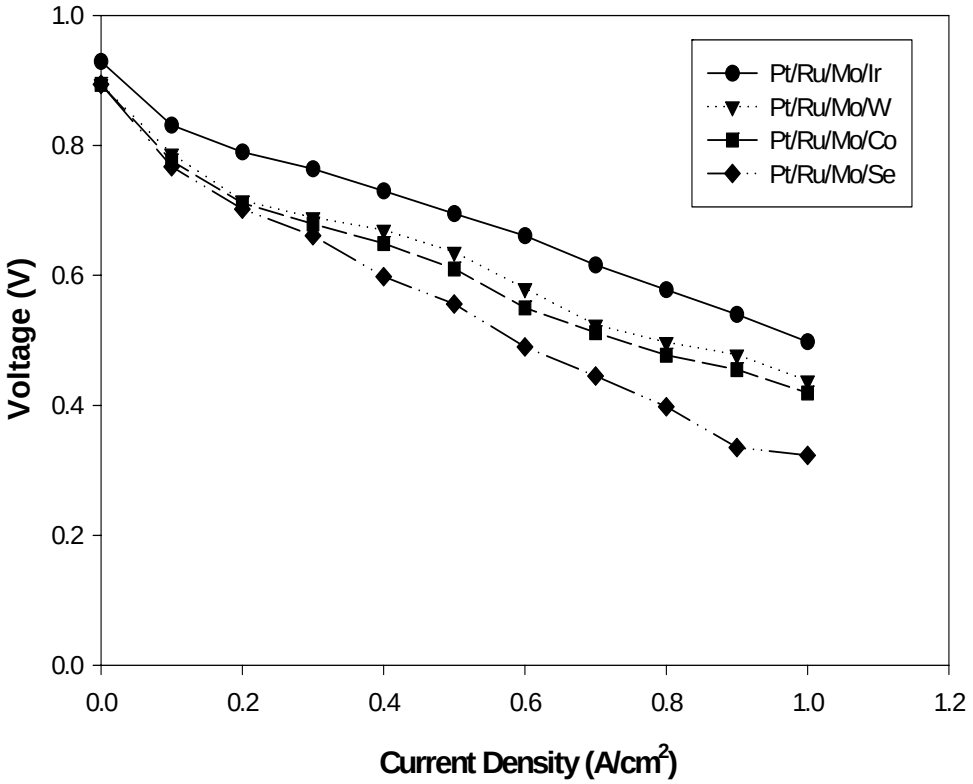

Figure 12. Current vs. voltage curves for quaternary metal (20 wt%) catalysts with pure H_2 in the feed stream

Figure 13 shows the comparison of quaternary metal catalysts made in this study and those made in a previous study from a similar method. The materials developed with sonication show a slightly better performance in the MEA for a given current density. With similar metal loadings, the sonication step dispersed the active metals more evenly along the active carbon support allowing for more active sites on the catalyst, thus giving a better electrical performance in the fuel cell.

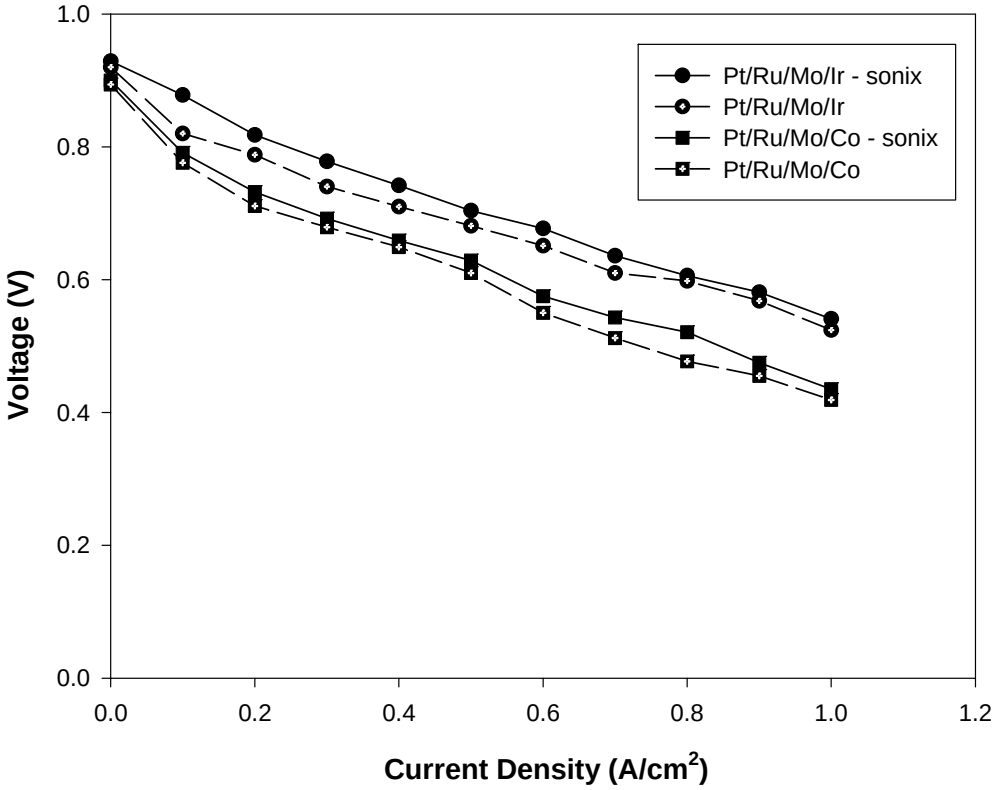

Figure 13. Performance comparison of current vs. voltage plots of quaternary metal (20 wt%) catalysts made with sonication and without sonication

CO Tolerance of Quaternary Metal Catalysts

The ability of a few of the ternary catalysts to oxidize carbon monoxide in the MEA leads to better CO tolerance in the fuel cell [16]. The quaternary metal catalysts chosen in this study were based upon the success of the Pt/Ru/Mo system, and exhibited notable CO tolerance in the MEA. Figure 14 shows the CO tolerance of the catalysts with 20 ppm and 100 ppm of CO in the hydrogen feed stream. Once again the overall performance of the fuel cell operating under reformate conditions did not increase significantly. The additions of the non noble metals Ir and W allowed for a lower platinum loading in the MEA. The transition metals Co and Se did not contribute to increasing the CO tolerance of the fuel cell. However, none of the MEAs made in this work exhibited a significant voltage output beyond 700 mA/cm^2 with 100 ppm of CO in the H_2-feed.

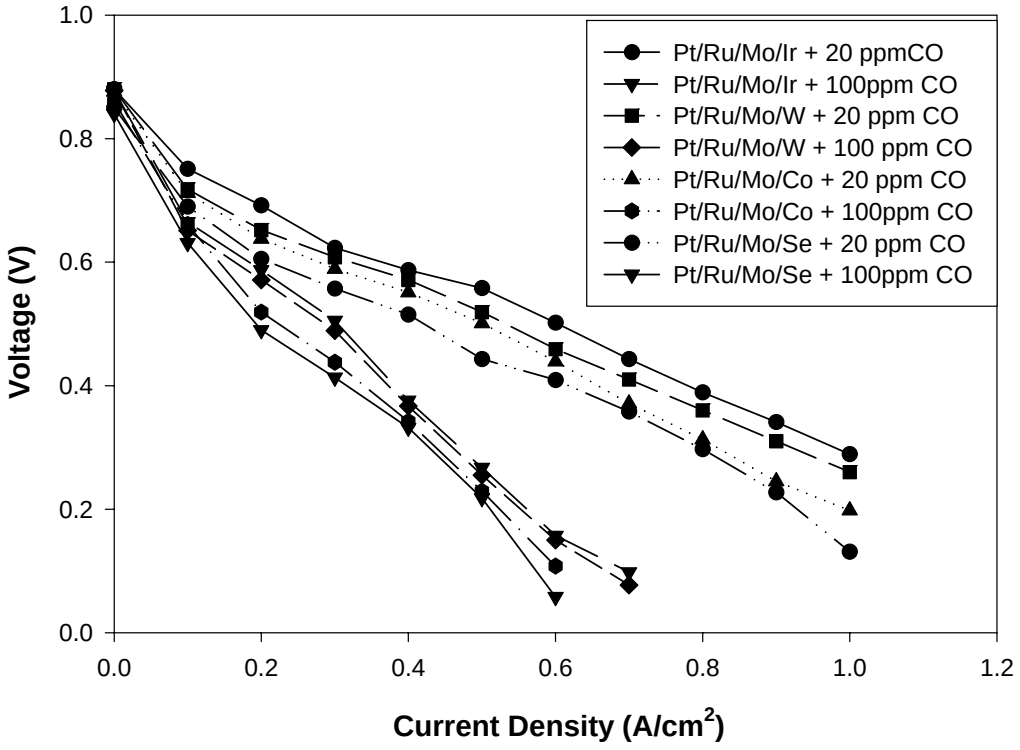

Figure 14. Current vs. voltage plots for quaternary metal (20 wt%) catalysts with 20 and 100 ppm of CO in the H_2-feed stream

Electrochemical Impedance Study

Until recently, electrochemical impedance spectra (EIS) were used only to evaluate the resistance and corrosion properties in other electrochemical devices such as batteries. More research is being conducted utilizing AC impedance to characterize the MEA of a PEM fuel cell. Raistrick et al. [18] have performed an extensive impedance study on the porous materials of the PEM fuel cell. They were able to develop a thin film model for the electrical circuit properties of the fuel cell. This model played a key role for future AC impedance studies of the PEM fuel cell. From this model other researchers were able to utilize EIS to study the effects of nafion loading, humidification and flooding, and CO tolerance in the MEA [19, 20]. In this work, electrochemical impedance was measured for a binary, ternary, and quaternary catalyst and their responses plotted on a Nyquist plot. Pure hydrogen was used in the anode and purified air was used in the cathode of the fuel cell for all AC impedance measurements.

Figure 15 shows the Nyquist plot for a commercial Pt/Ru catalyst (Electrochem Inc.) made into an MEA and tested in the laboratory at three different voltages. A Nyquist plot of an in-house Pt/Ir/C catalyst is shown in Figure 16 at two different voltages.

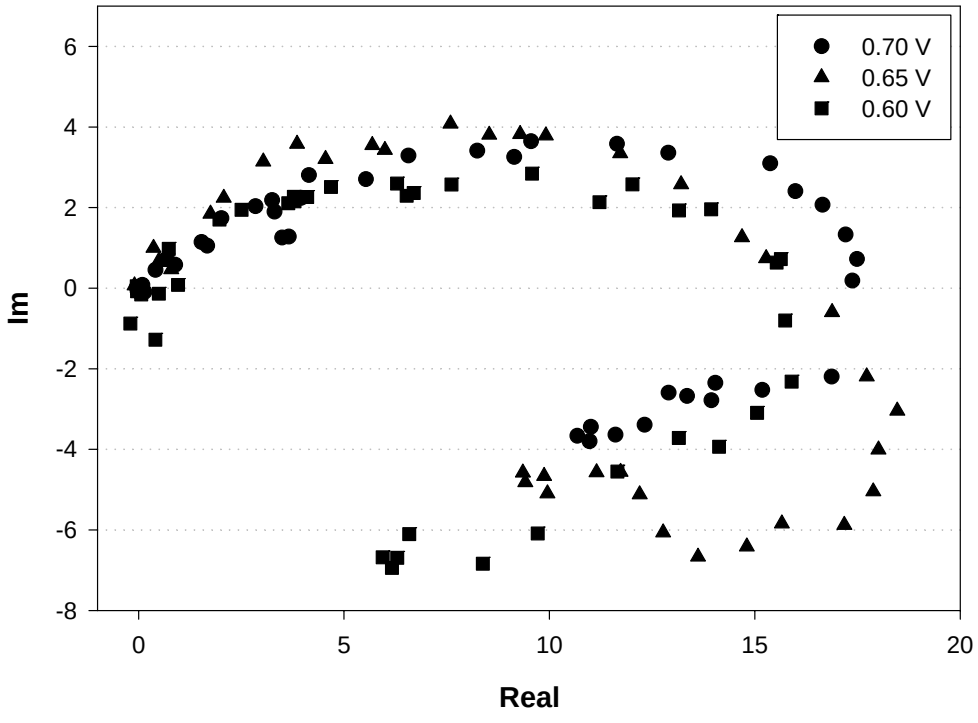

Figure 15. Nyquist plot of a commercial Pt/Ru/C catalyst

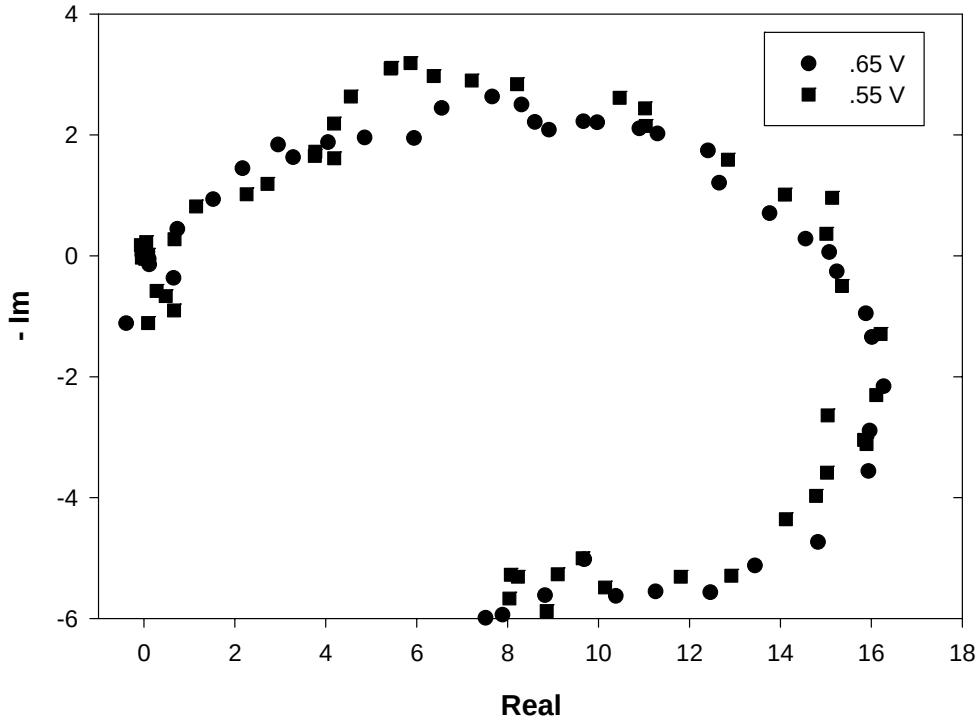

Figure 16. Nyquist plot of an in-house Pt/Ir/C catalyst

There is no difference in the values and shapes of the graphs of the in-house binary catalyst and that of the commercial binary catalysts. The Pt/Ru/C catalyst has a more defined response in the higher frequency region. This is the impedance response between 1000 Hz and 10,000 Hz, and is located in quadrant IV of the plots. Both plots have approximately the same arc radius in the first quadrant of the graph which can be correlated to the charge transfer resistance in the porous electrode [21]. This shape in the Nyquist plot gives information on the resistance properties and fluid mechanics taking place in the MEA.

Every type of electrical circuit gives a different shape in the impedance response when plotted as a Nyquist plot (also known as Common Equivalent Circuit Models) [22]. Electrochemical impedance spectra data is generally analyzed in terms of an equivalent circuit model. The MEAs presented here have responses that are similar to a Randles Cell and a Mixed Kinetic and Diffusion Control circuit model. This is based on the shape and size of the arcs in the Nyquist plots of the catalysts.

Figures 17 and 18 give the impedance responses of the ternary Pt/Ru/Mo and quaternary Pt/Ru/Mo/Ir/C catalysts. The circuit model previously given applies to these electrodes as well. One common characteristic of this type of electrode is the double layer capacitance or surface charging taking place in the structure of the MEA. One of the major differences in the Nyquist plot of the ternary and quaternary catalysts from their binary counterparts is the response in the high frequency range. There is not the large arc below the x-axis and the height of the arc in the first quadrant. The thin film diffusion effects are consistent for both catalysts as well. At low overpotentials, the dc current completely penetrates the pores and the potential is uniform [18].

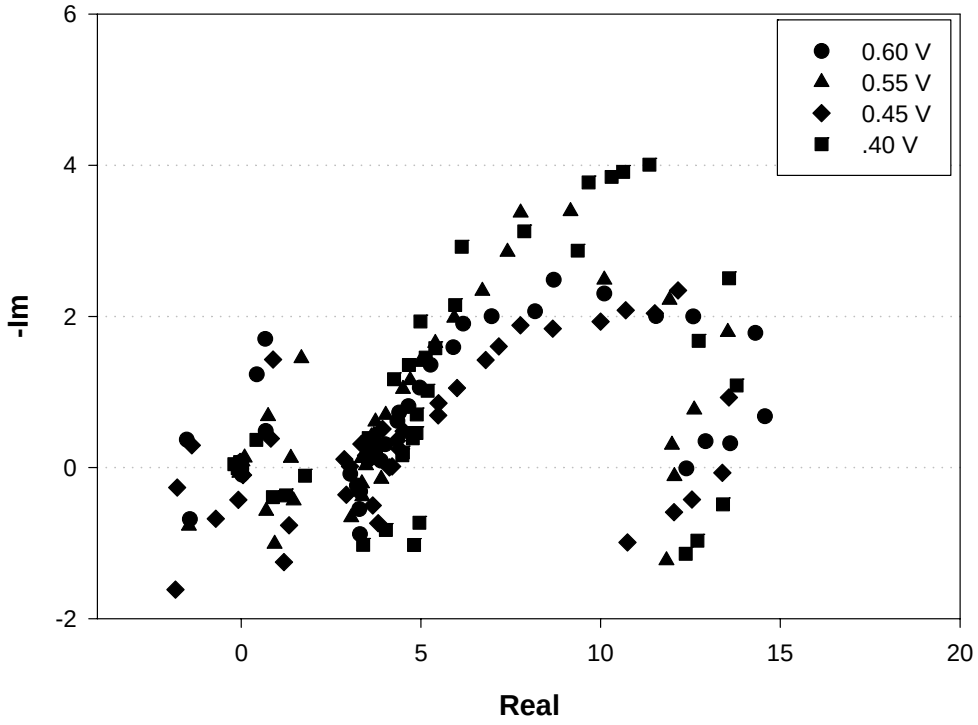

Figure 17. Nyquist plot of an in-house Pt/Ru/Mo/C catalyst

The high frequency response in the Nyquist plot of the quaternary catalyst differs from the ternary and binary catalyst. The high frequency portion of the graph is located near the origin of the y and x axis. In this region there is a smaller semicircle in front of the larger semicircle. This type of response is typical for a cell with mixed kinetic and charge transfer control. This is a cell where polarization is due to a combination of kinetic and diffusion processes in the electrode.

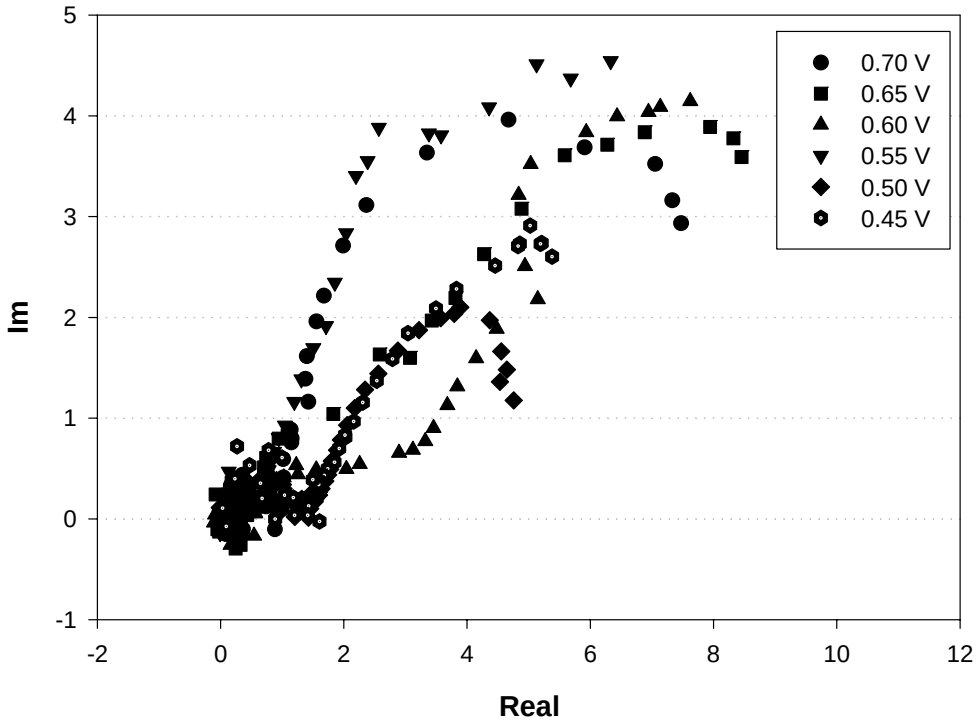

Figure 18. Nyquist plot of an in-house Pt/Ru/Mo/Ir/C catalyst

Cost of Electrocatalysts

Given the electrochemical performance of the materials, it is important to analyze the cost of each catalyst in order to understand which candidate would be most economical to use in the PEM fuel cell. Table 4.2 shows the costs of producing 100 grams of the alloyed catalyst and the pure platinum on carbon catalyst. The cost of the Pt/C catalyst is more than any of the binary, ternary, or quaternary Pt-based electrocatalysts synthesized in-house. When comparing the cost and the performance of the materials, the ternary Pt/Ru/Mo/C catalyst would be the economical choice for use in the fuel cell because it combines performance with a relatively low cost.

H_2S Tolerance of Pt-alloy Catalysts

The Pt-based binary, ternary and quaternary catalysts of Ru, Mo, and Ir performed very well in MEAS anode in presence of CO contaminant in hydrogen fuel. In an attempt to test these catalysts in presence of H_2S contaminant at 20 ppm, we had difficulty in getting reproducible polarization curve and the results are reported here. The test cell performance was not stable. Why this happened, needs further investigation.

Table 2. Cost of Producing 100g of catalyst**.**

Pt/C Cost	Binary Catalyst	Cost	Ternary Catalyst	Cost	Quaternary catalyst	Cost
$20.16	Pt/Ru/C	$15.06	Pt/Ru/Mo/C	$10.16	Pt/Ru/Mo/Ir/C	$12.13
	Pt/Mo/C	$10.19	Pt/Ru/Ir/C	$16.18	Pt/Ru/Mo/W/C	$7.88
	Pt/Ir/C	$19.17	Pt/Ru/W/C	$10.48	Pt/Ru/Mo/Co/C	$8.43
	Pt/W/C	$10.66	Pt/Ru/Co/C	$11.22	Pt/Ru/Mo/Se/C	$8.05
	Pt/Se/C	$11.01	Pt/Ru/Se/C	$10.71		

CONCLUSIONS

The development of novel platinum-based electrocatalysts plays a very important role in the production of high performance PEM fuel cells for commercial applications. Cost reduction and ultra pure hydrogen production are major obstacles to overcome in order for the technology to become a mainstream application. In this work low platinum loading electrocatalysts were synthesized and improved upon for testing in a single PEM fuel cell. The materials were evaluated physically through SEM, and electrochemically through polarization measurements and AC impedance tests. Figure 19 shows the comparison of the binary, ternary, and quaternary catalysts made in this work to a commercial Pt/C catalyst. Not only was the amount of platinum decreased in the MEA but the overall performance of the fuel cell was enhanced. It can be concluded that the synthesis method employed successfully dispersed the active metals on the carbon support and increased the electrical performance of the cell while maintaining a platinum loading less than 0.4 mg/cm^2 for each catalyst. The CO tolerance of the MEA was also enhanced when compared to a commercial MEA as seen in Figure 20. The CO tolerance of the fuel cell at 20 ppm is considerably greater for the Pt/Ru/Mo and Pt/Ru/Mo/Ir catalysts developed in-house.

Based on the analysis of the materials and fuel cell performances the following conclusions can be made:

- The modified synthesis method successfully alloyed non-noble metals Ir, Mo, W, Co and Se with platinum and dispersed them more evenly along the active carbon support as confirmed by SEM.

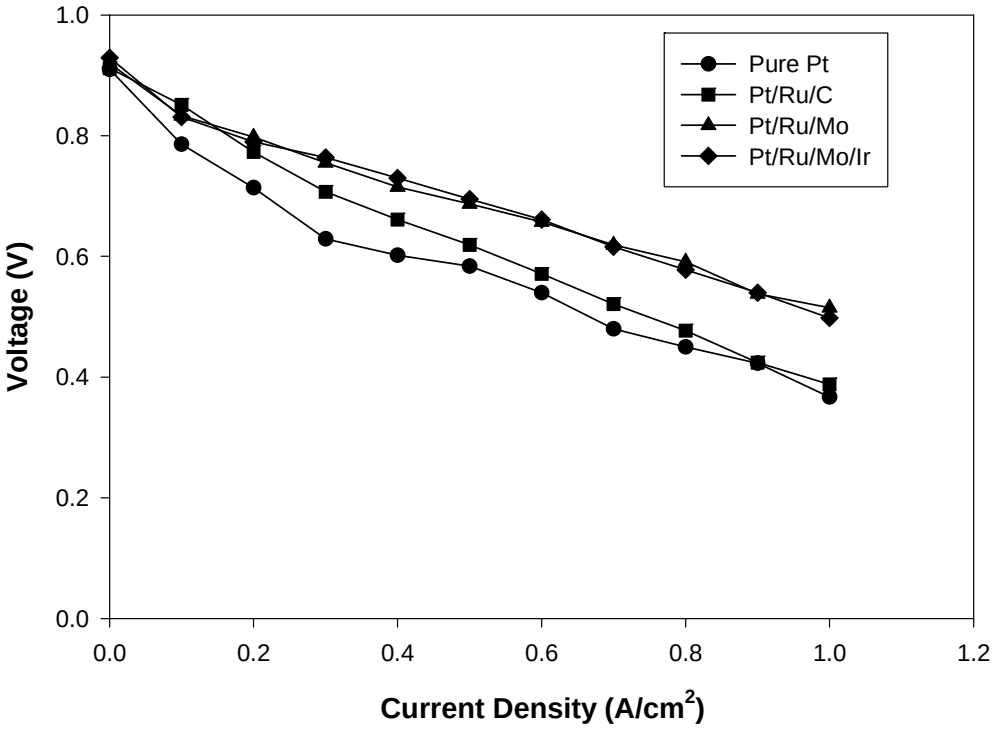

Figure 19. Comparison of current vs. voltage curves for in-house binary, ternary and quaternary (20 wt%) catalysts and a commercial Pt-based MEA in pure H_2-feed

- The addition of ultrasonication in the synthesis step improved the electrical performance of the fuel cell when compared to similar catalysts made in a previous work.
- The Pt/Ru/Mo/C and Pt/Ru/Mo/Ir/C catalysts showed a better CO tolerance when compared to the other in-house catalysts with 20 ppm and 100 ppm of CO in the feed stream.
- The Pt/Ru/Mo/Ir/C and Pt/Ru/Mo/C catalysts exhibited superior performance in the fuel cell with pure H_2 and contaminated H_2 in the feed when compared to a commercial Pt/C MEA.
- Nyquist ac impedance plots of Pt/Ir/C, Pt/Ru/Mo/C, and Pt/Ru/Mo/Ir catalysts exhibited similar properties to those previously reported for porous materials utilized in a PEM fuel cell.

In order to develop low platinum loading, and thus low cost CO-tolerant catalysts, one should incorporate metals that have similar physical and chemical properties to platinum.

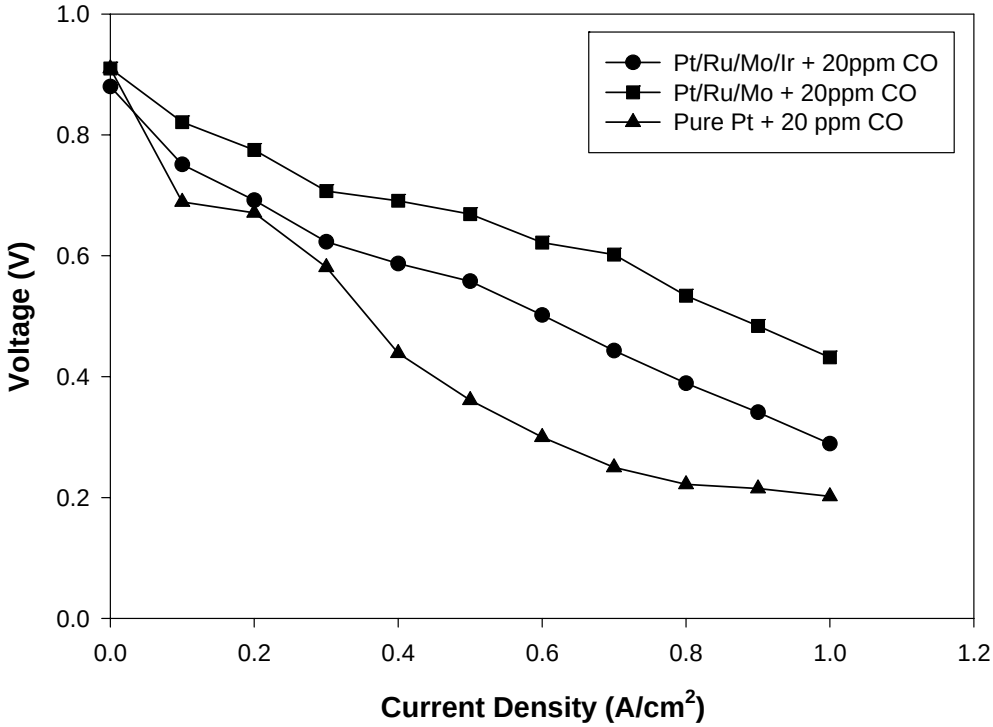

Figure 20. Comparison of current vs. voltage curves for in-house ternary and quaternary (20 wt%) catalysts and commercial Pt/C MEA with 20 ppm of CO in the H_2-feed stream

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